

**SPECIATION OF MERCURY IN DIFFERENT  
ENVIRONMENTAL COMPARTMENTS.  
DESIGN, DEVELOPMENT AND OPTIMIZATION OF  
ANALYTICAL METHODS AND PROCEDURES.**

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**A dissertation submitted to the faculty of science, University of Witwatersrand, in  
fulfilment of the requirements for the degree of Master of Science.**

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## **Declaration**

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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(Signature of Candidate)

\_\_\_\_\_ Day of \_\_\_\_\_ 2009

## Abstract

The widespread use of organometallic compounds and their subsequent release into the environment has created a great environmental concern about the toxicity and effects of these pollutants. Mercury pollution is a growing concern worldwide because it can reach high concentrations in various environmental media and thus adversely affect humans, wildlife and ecosystem functioning.

Mercury is present in the environment in different molecular forms with specific biogeochemical transformation and ecotoxicity. Inorganic  $\text{Hg}^{2+}$  is the main form in water and sediment samples. Concentration levels of organomercury species is very low (usually  $\text{ng L}^{-1}$ ) in aquatic environments but the toxic effect of these compounds can be significant due to their tendency for bioaccumulation and biomagnification in the food chain.

The development of a sensitive, reliable, simple, and cost effective procedure for speciation analysis of mercury in different environmental compartments is currently one of the principal research challenges in environmental analytical chemistry. To this end, this study aimed to develop and optimize analytical methods and procedures for the determination of total mercury and the speciation of inorganic and organic forms of mercury. The hyphenation of gas chromatography and inductively coupled plasma mass spectrometry (GC-ICP-MS) was achieved and used successfully.

Rapid and efficient sample preparation procedures based on microwave-assisted extraction for solid samples were developed. The optimized analytical methods and procedures were validated by the analysis of environmental certified reference materials (CRM 015-050 sediment for  $\text{Hg}_{\text{TOT}}$  and CRM 463 tuna fish for  $\text{Hg}_{\text{TOT}}$  and MeHg).

The developed methodologies were finally applied to real environmental samples, namely soil, sediment, water, fish and human hair, collected in some South African regions affected by environmental pollution due to reprocessing of old tailings dumps and chlor-alkali facilities. The study included collection of ancillary data (pH, redox potential) which are critically important for mercury monitoring program. Predictive models of mercury speciation in water samples based on thermodynamic solution equilibria were also established.

## **Dedication**

To Mickel-Ange Lusilao

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## **ABBREVIATIONS**

**AAS:** atomic absorption spectrometry

**AFS:** atomic fluorescence spectrometry

**BCR:** Community Bureau of Reference

**CE:** Capillary electrophoresis

**CNRS:** Centre national de recherche scientifique

**CRM:** certified reference material

**CV:** cold vapor

**CVG:** chemical vapor generation

**CVT:** cold vapor technique

**CZE:** capillary zone electrophoresis

**Eth:** Ethylation

**FOREGS:** Forum of the European Geological Surveys

**GC:** gas chromatography

**GC-ICP-MS:** gas chromatography- inductively coupled plasma-mass Spectrometry

**GPS:** Global Positioning System

**HG:** hydride generation

**HgEt<sub>2</sub>:** Diethylmercury

**Hg-P:** particulate-bound mercury

**HPLC:** high-performance liquid chromatography

**ICP-MS:** inductively coupled plasma-mass spectrometry

**IDMS:** isotope dilution mass spectrometry

**IHg:** inorganic mercury

**IPCS:** International Programme on Chemical Safety

**LC:** liquid chromatography

**LCABIE:** Laboratoire de chimie analytique bio-inorganique et environnement

**LOAEL:** lowest-adverse-affect-effect-level

**LOD:** Limit of detection

**LOQ:** Limit of quantitation

**MAE:** microwave-assisted extraction

**MCL:** maximum contaminant level

**MeHg:** monomethylmercury

**MeHgEt:** Methylethylmercury

**MIP-AES:** microwave-induced plasma atomic emission spectrometry

**MRC SA:** Medical Research Council South Africa

**MS:** mass spectrometry

**NaBEt<sub>4</sub>:** sodium tetraethylborate

**NOAEL:** no-adverse-affect-effect-level

**QC:** quality control

**RfD:** reference dose

**RGHg:** reactive gaseous mercury

**RSD:** Relative standard deviation



**SA:** South Africa

**SABS:** South African Bureau of Standards

**SAWQG:** South African Water Quality Guidelines

**SEM:** secondary electron multiplier

**SFE:** supercritical fluid chromatography

**TDI:** tolerable daily intake

**TMAH:** Tetramethylammonium hydroxide

**USEPA:** United States Environmental Protection Agency

**WHO:** World Health Organization

